Photoinduced phase transition probed by time-resolved X-ray diffraction

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Groupe Matière Condensée et Matériaux, France

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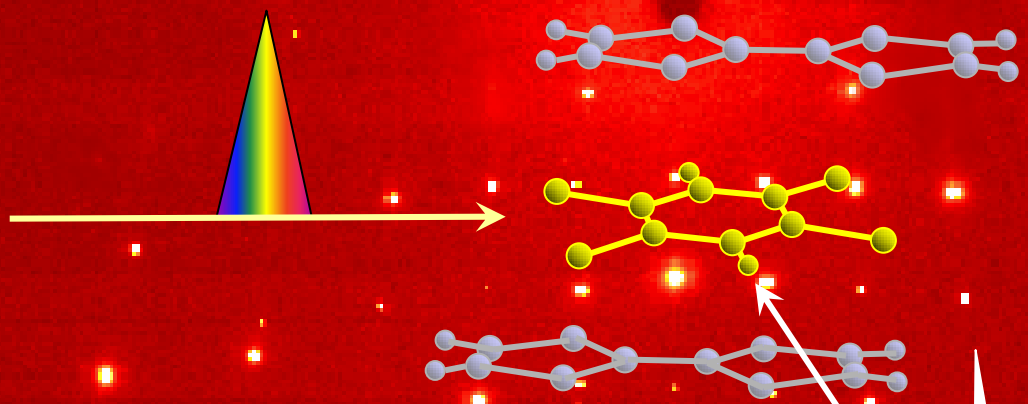


Structurale investigation of photo-induced phase transition

L. Guérin, M. Buron, M.H. Lemée-Cailleau, H. Cailleau,

Groupe Matière Condensée et Matériaux, University of Rennes 1, France

Investigation of photo-induced phase transition by pump-probe experimen

S. Koshihara,

ERATO project JST, Tokyo Inst of Technology, Japan

100 ps time-resolved experiments at the ESRF

M. Wulff, S Techert, A Plech

ID09B Team, ESRF, France

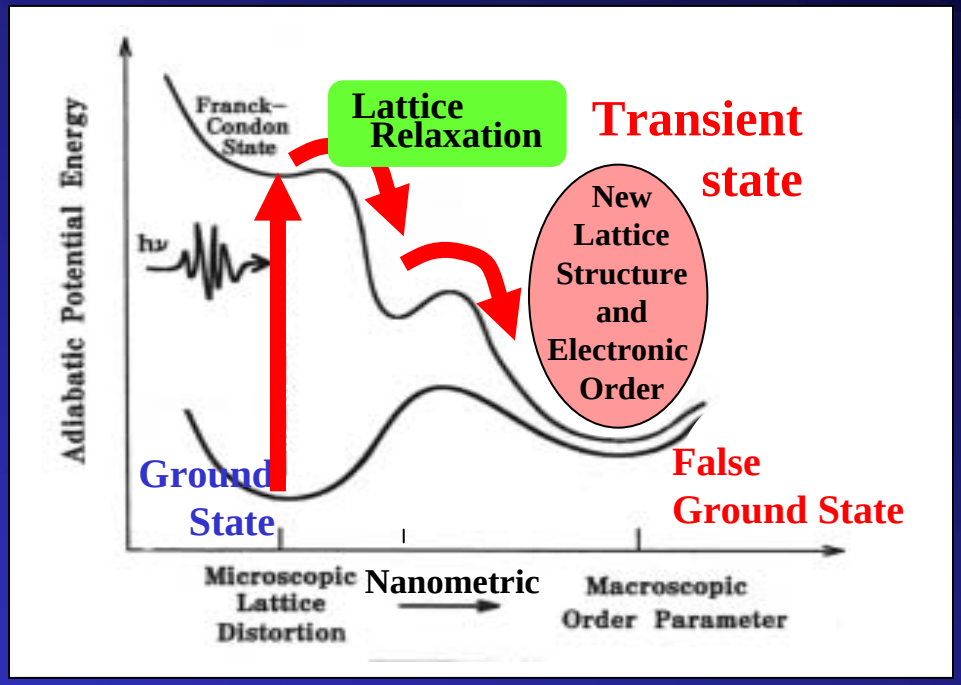
Photoinduced solid state phase transition

Out of equilibrium and multi-scale process in solids

Self-amplification of excited state

K. Nasu (2001)

J. Phys.: Condens. Matter.

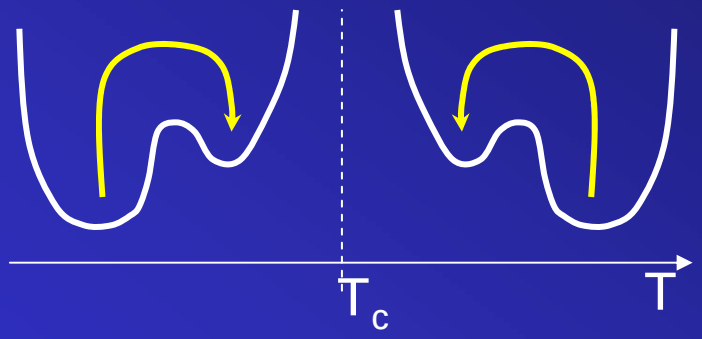


High density electronic excitation triggering structural instability :

insulating ⟶ metal

insulating ⟶ insulating

Solid state molecular switching



Which kind of information one can get from the diffracted X-ray?

for a given cell n $F_n = \langle F \rangle + \Delta F_n$

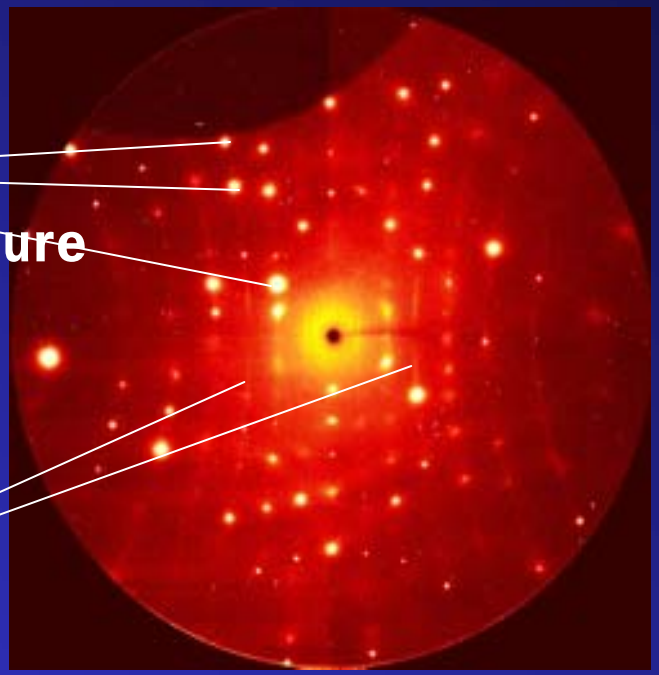
$$I(\mathbf{q}) = \underbrace{N^2 \left|\langle F \rangle\right|^2 . \sum_{hkl} \left|\delta(\mathbf{q} - \mathbf{Q}_{hkl})\right|^2}_{\text{Diffraction}} + \underbrace{N' \sum_m \left\langle \Delta F_n^* \Delta F_{n+m} \right\rangle e^{-i\mathbf{q}.\mathbf{r}_m}}_{\text{Diffuse scattering}}$$

Bragg peaks : Diffraction

position : average lattice

shape : domain size

intensity : atoms and average structure



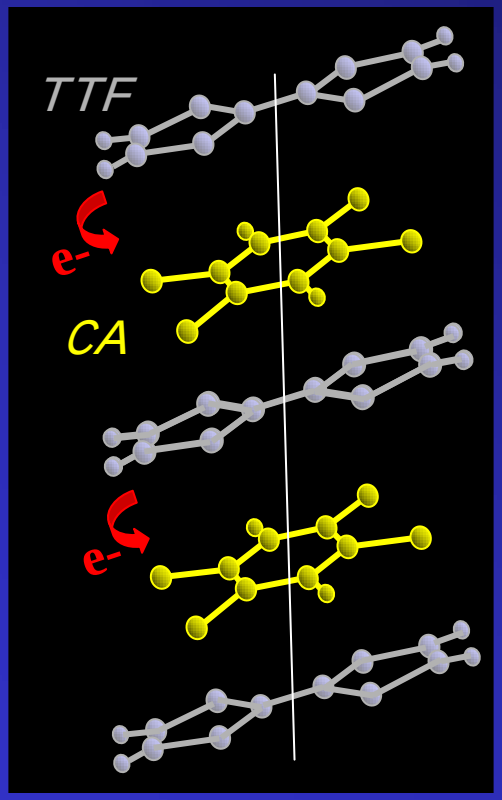
Diffuse scattering :

position : local periodic structure

shape : correlation of local order

intensity : deviation from the average structure

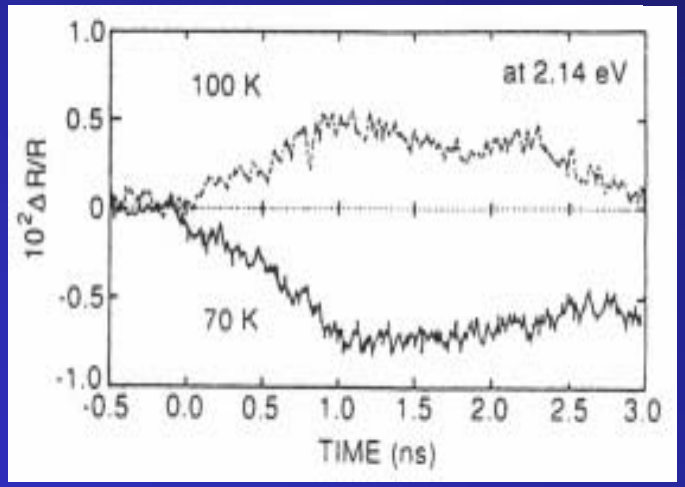
PHASE TRANSITION IN CT MOLECULAR SYSTEMS

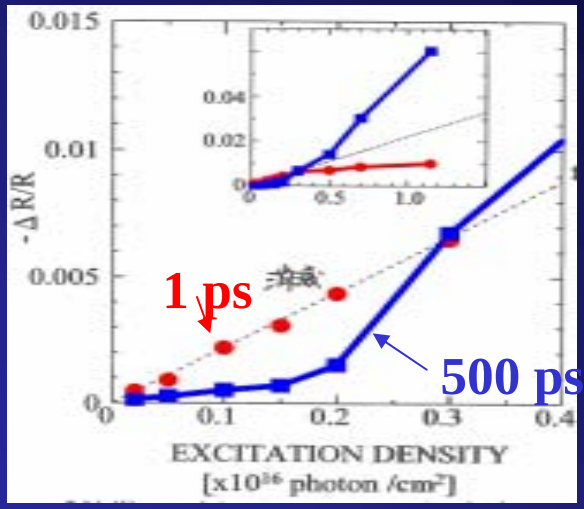


IONIC low T phase T° **NEUTRAL high T phase**

81 K

PHOTOINDUCED PHASE TRANSITION

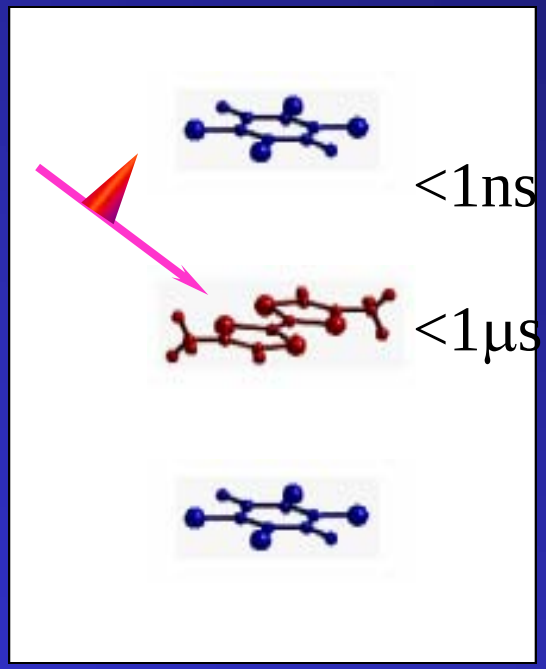


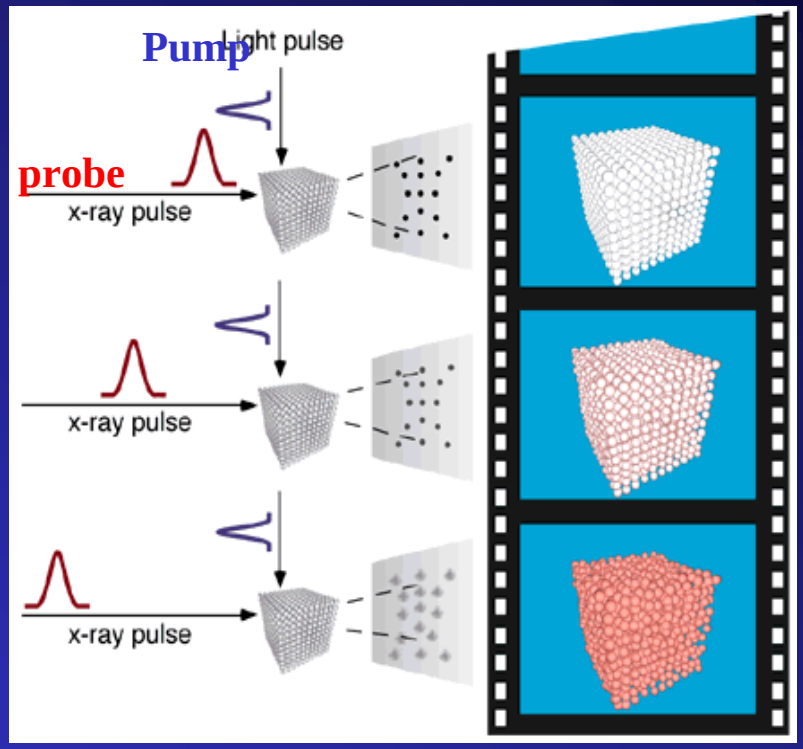


S. Koshihara et al, J. Phys. Chem. (1999)Okamoto et al,PRL(2002)

- **Highly cooperative : few 100 molecules / photon**
- **very fast : few 100 ps**
- **Highly non-linear : threshold behavior and $h\nu_{pump}$ dependence**

TIME-RESOLVED CRYSTALLOGRAPHY





X-ray sources :

- synchrotron

  -> 50-150 ps

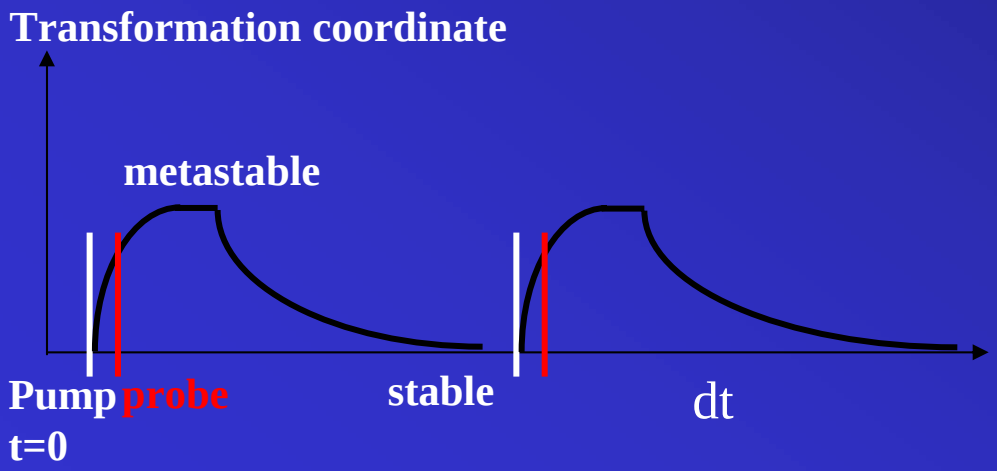
  -> 100 fs

- Laser systems

  -> 100 fs

- Future sources

  -> 100 fs



stroboscopic techniques

'Watching matter rearrange'
K. Nelson Science (1999)

Molecular movies

PICOSECONDE CRYSTALLOGRAPHIC MEASUREMENTS: ID09B ESRF

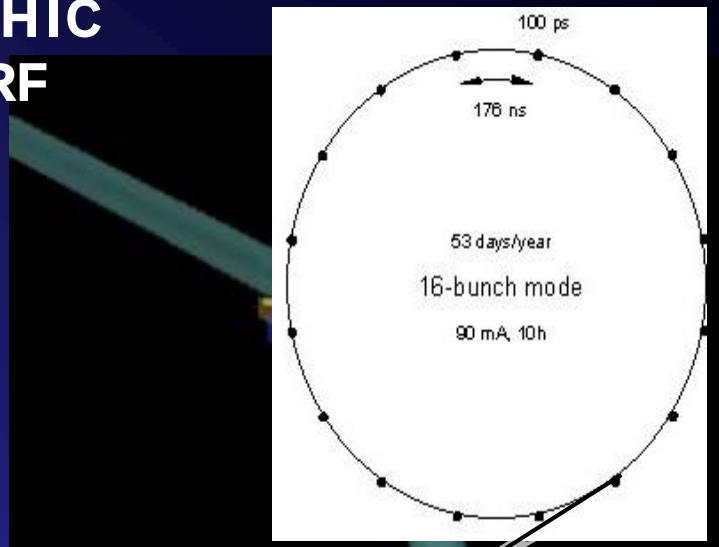
. Time structure of the synchrotron radiation :

pulse width : 100 ps

repetition rate : 1kHz (896.6 Hz)

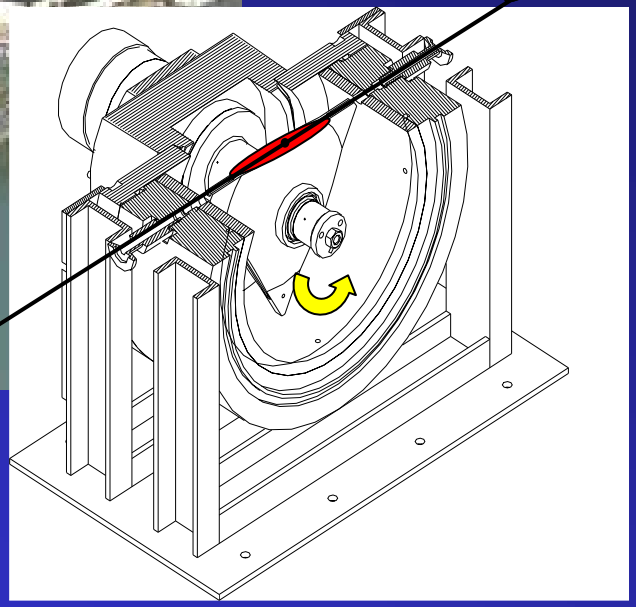
select 1 pulse over 6400 !

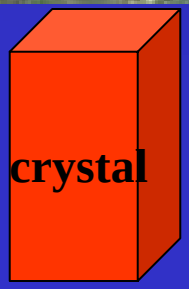
. Synchronisation chopper/Laser

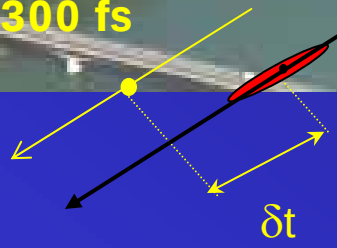


Ruby Pulse
100 ps

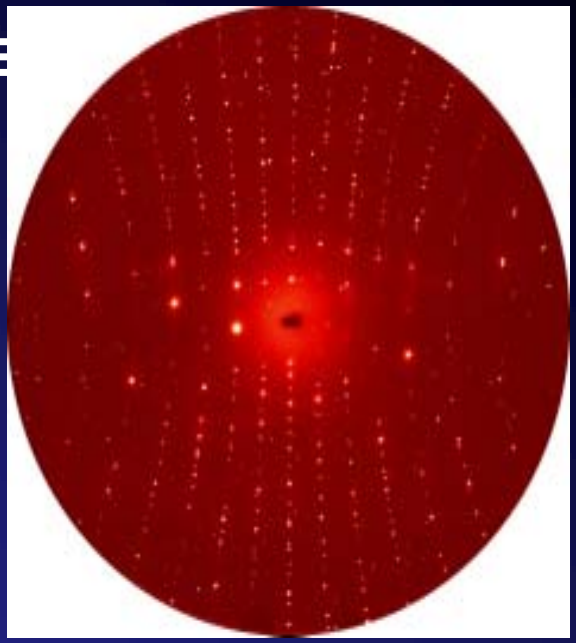
Laser
pump
300 fs





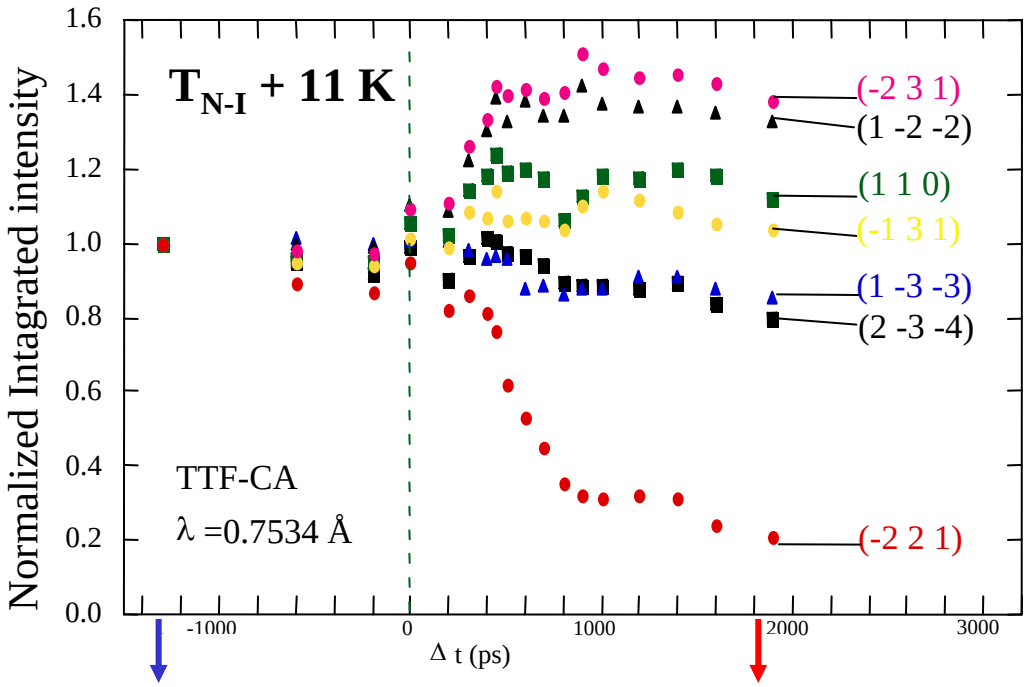


STRUCTURAL STUDY OF THE PHOTO-INDUCE
N-I TRANSITION: TTF-CA
pump -Xray probe experiment ID09 ESRF



X-ray Pulses 100 ps

1st monochromatic experiment



Neutral state (high temperature)

Pulse laser 300 fs λ=800 nm

Ionic state (photo-induced)

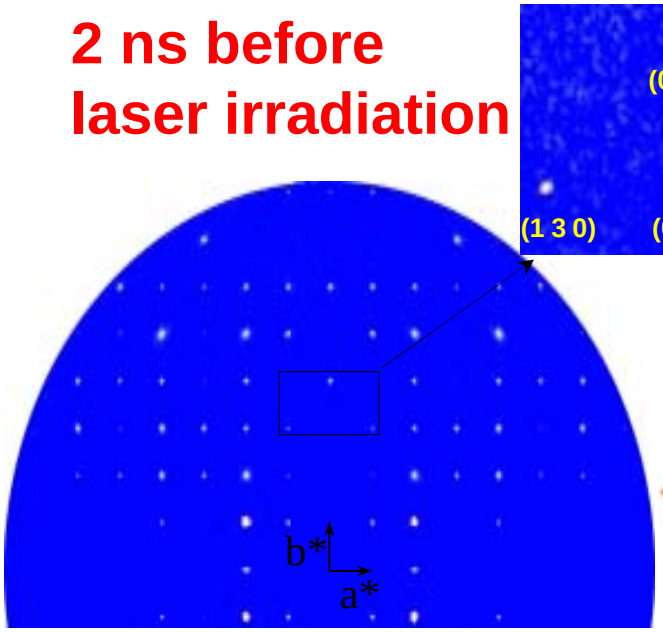
Structural reorganization :
3D domains
Large part transformed

E. Collet et al, Science 300 612 (2003)

PHOTO-INDUCED STRUCTURAL ORDER

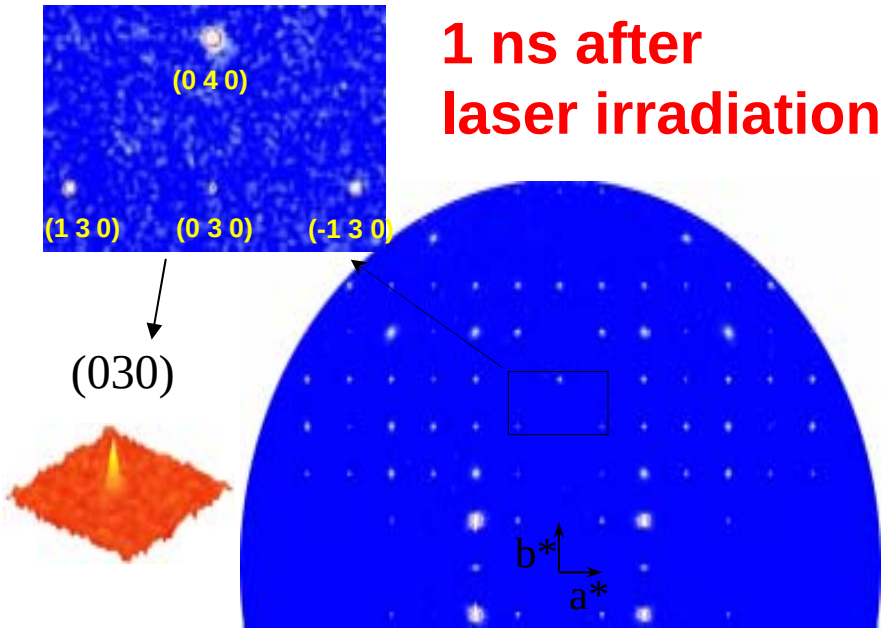
Complete data collection : scattered intensity in the reciprocal space

2 ns before laser irradiation



no (030)

1 ns after laser irradiation



(030)

Neutral phase

Space group **$P2_1/n$**

(0 k 0) : k = 2n+1 **absent**

(h 0 l) : h+l = 2n+1 **absent**

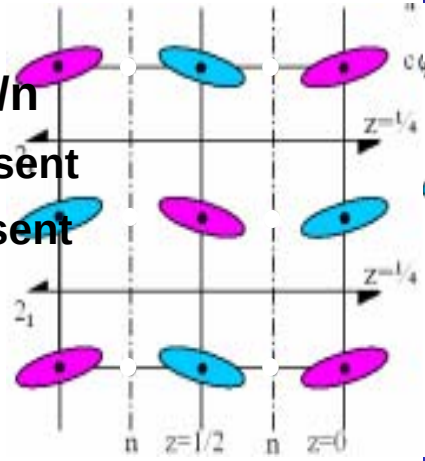
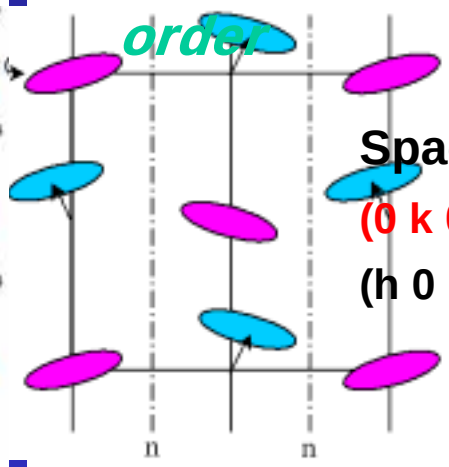


Photo-induced ferroelectric order



Space group **Pn**

(0 k 0) : k = 2n+1 **present**

(h 0 l) : h+l = 2n+1 **absent**

E. Collet et al, Science 300 612 (2003)

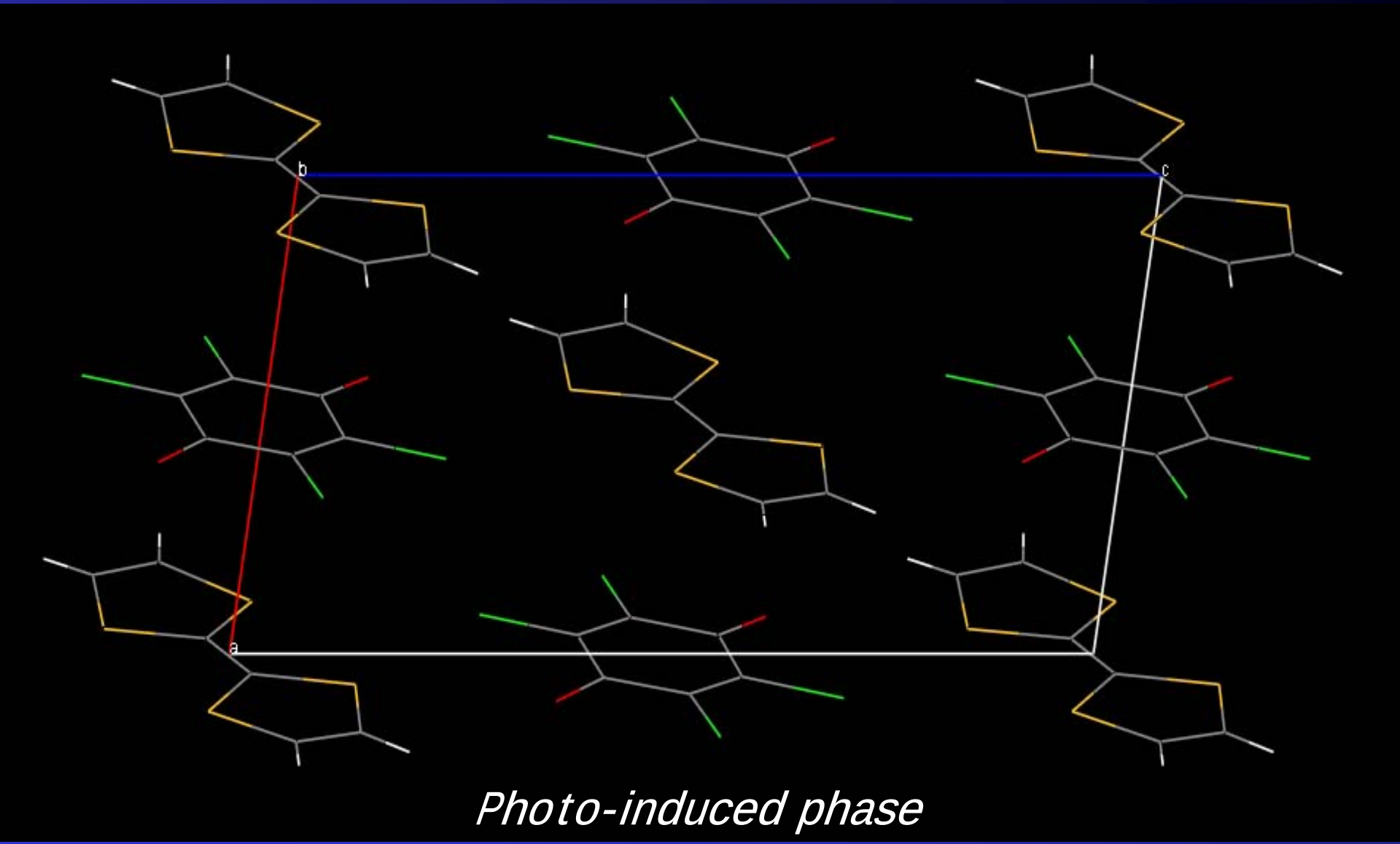
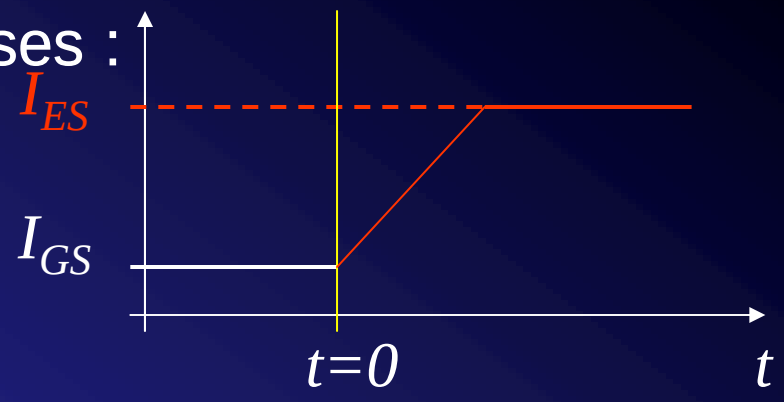


Photo-induced phase

Nucleation VS homogeneous processes : meaning of the change of intensity



Coherent motion of atoms

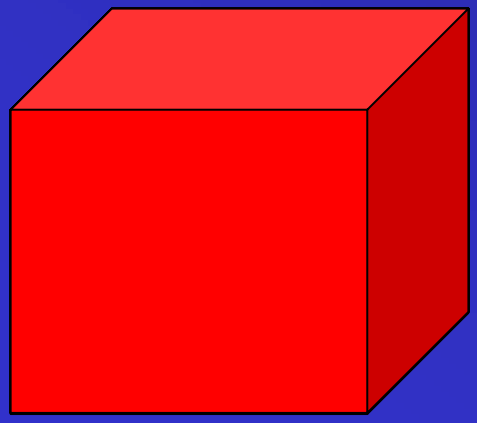
change of the structure factor over the volume

$$F_{hkl} \rightarrow F_{photo}(\Delta t)$$

and *intensity*

$$I_{GS}(hkl) \rightarrow I_{photo}(\Delta t)$$

Can be ultra-fast

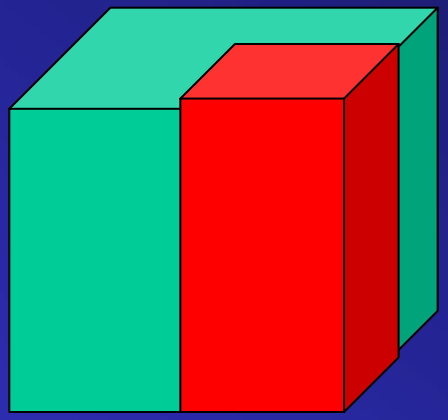


Nucleation of the excited domain

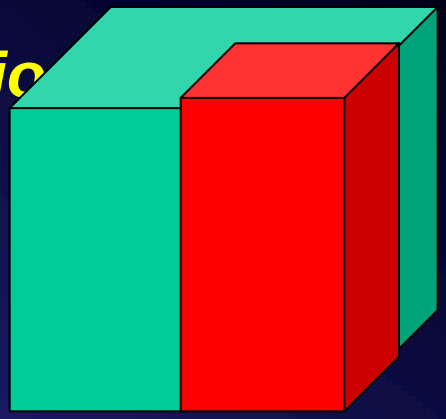
with volume fraction x

$$I(\Delta t) = (1-x(\Delta t))I_{GS} + x(\Delta t)I_{photo}(\Delta t)$$

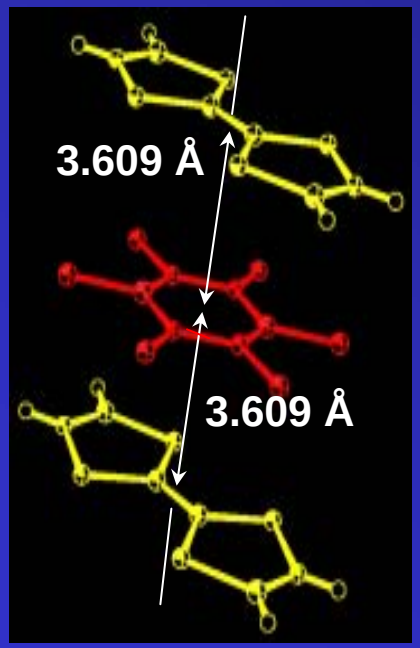
Speed limited



Crystal structure with 100 ps time resolutio refinement of homogeneous state

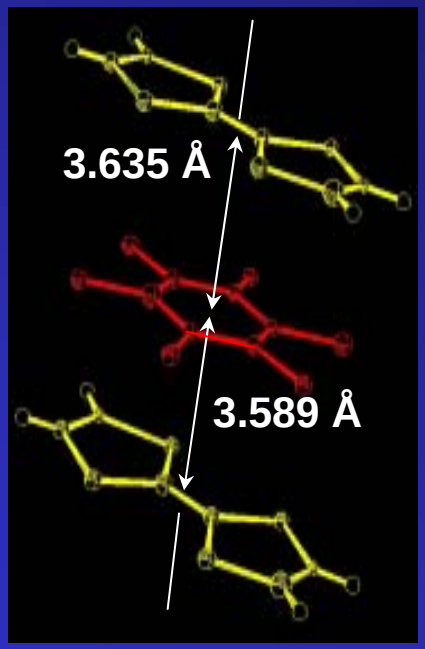


Δt= -2 ns



N phase

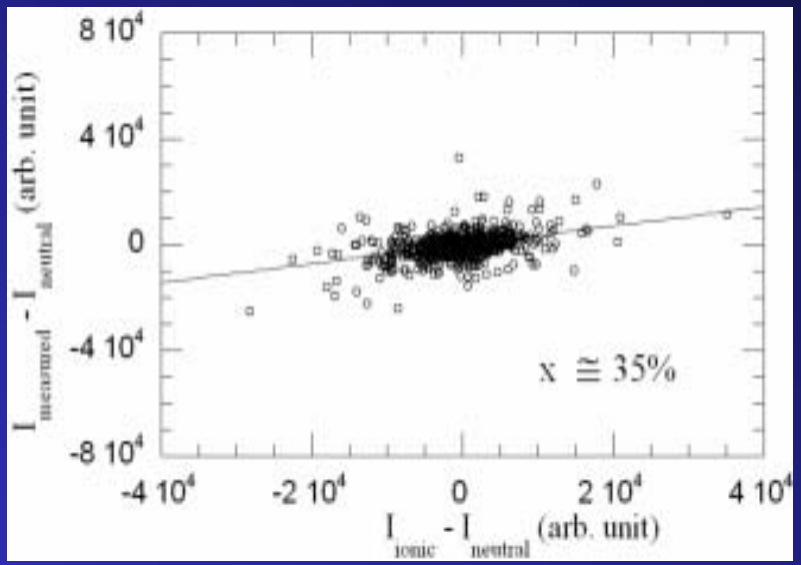
Δt= +1 ns



I photo-induced ferroelectric state

coexistence of N_{para} and I_{ferro} phases

$$I(hkl) = X\ I_{Iferro}(hkl) + (1-X)\ I_N(hkl)$$



X = 35 %

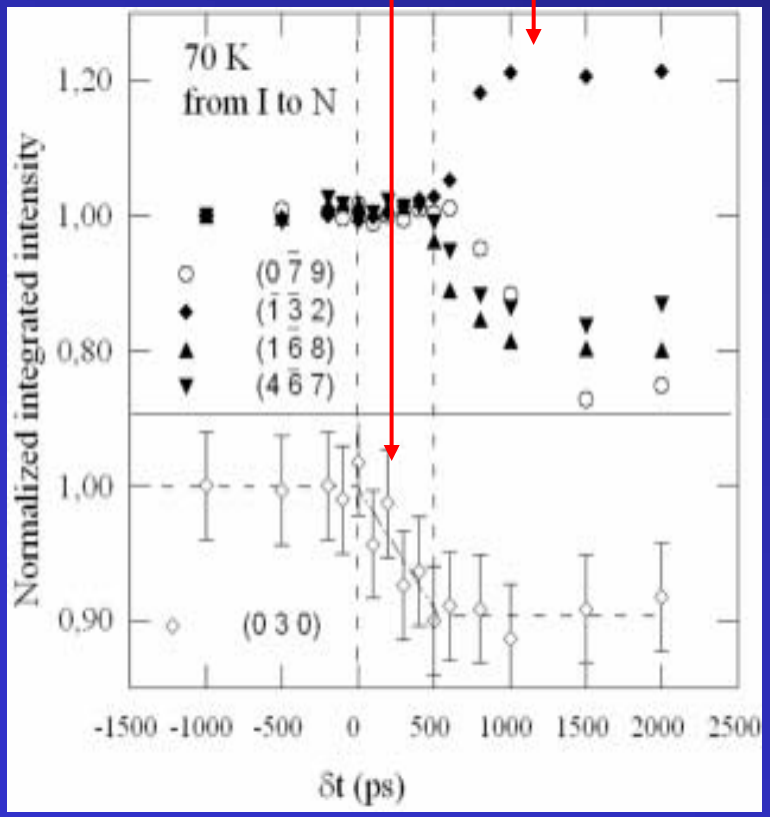
Lost of inversion center due to dimerization process

L. Guerin et al, Chem Phys (2004)

Opposite I-to-N photo-induced transformation : TTF-CA 70 K

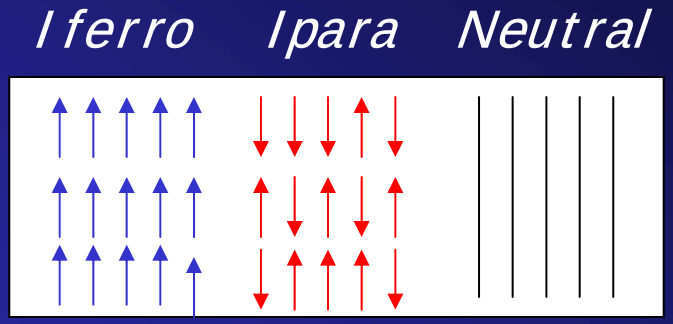
- intermediate disordered state ?

Change of symmetry + Change of state



L. Guérin, et al, Chem Phys. Special issue (2004)

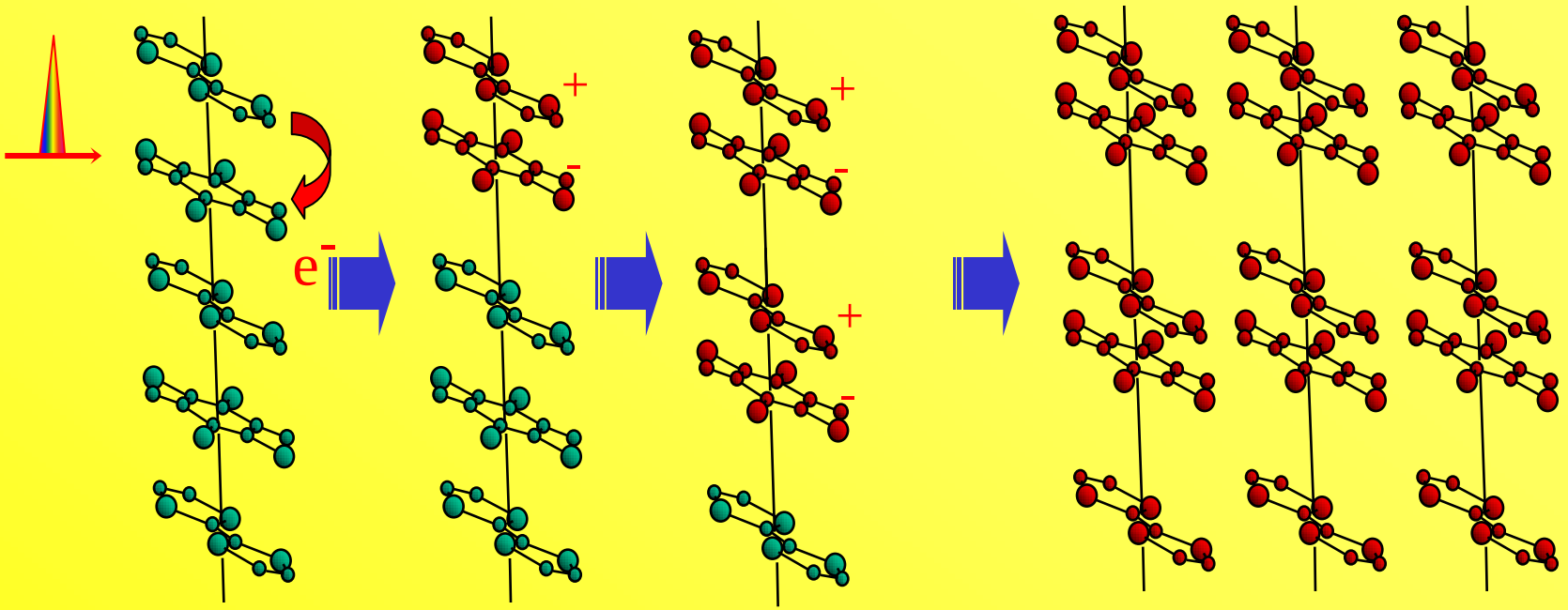
Phase diagram at thermal equilibrium



T. Luty et al, Europhysics Lett., 59 (2002)

M.H. Lemée-Cailleau et al, PRL 79 1690 (1997)

What is the mechanism???



100 fs-1 ps

100 ps

photoinduced cooperative molecular switching along the chain : 1D process

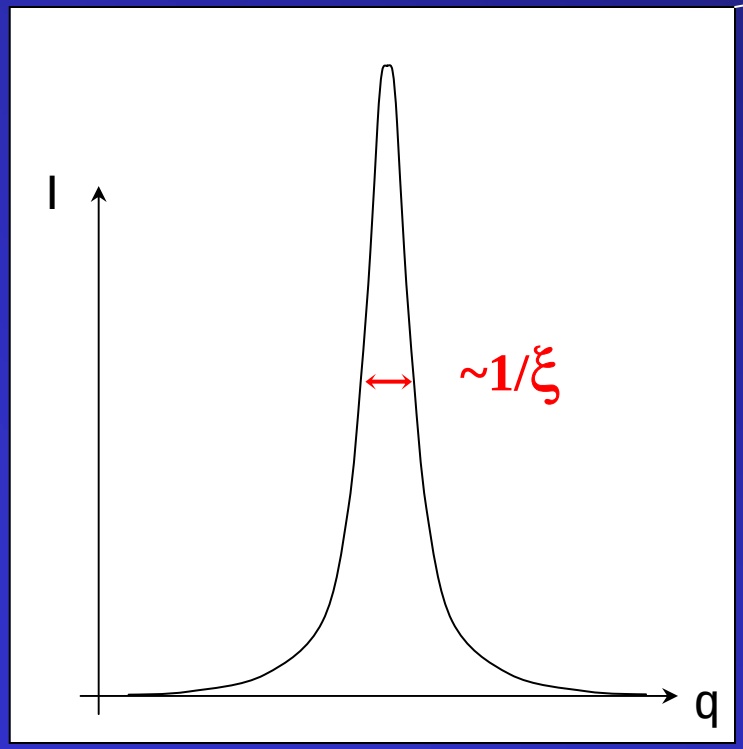
3D ordering of ionic dimers

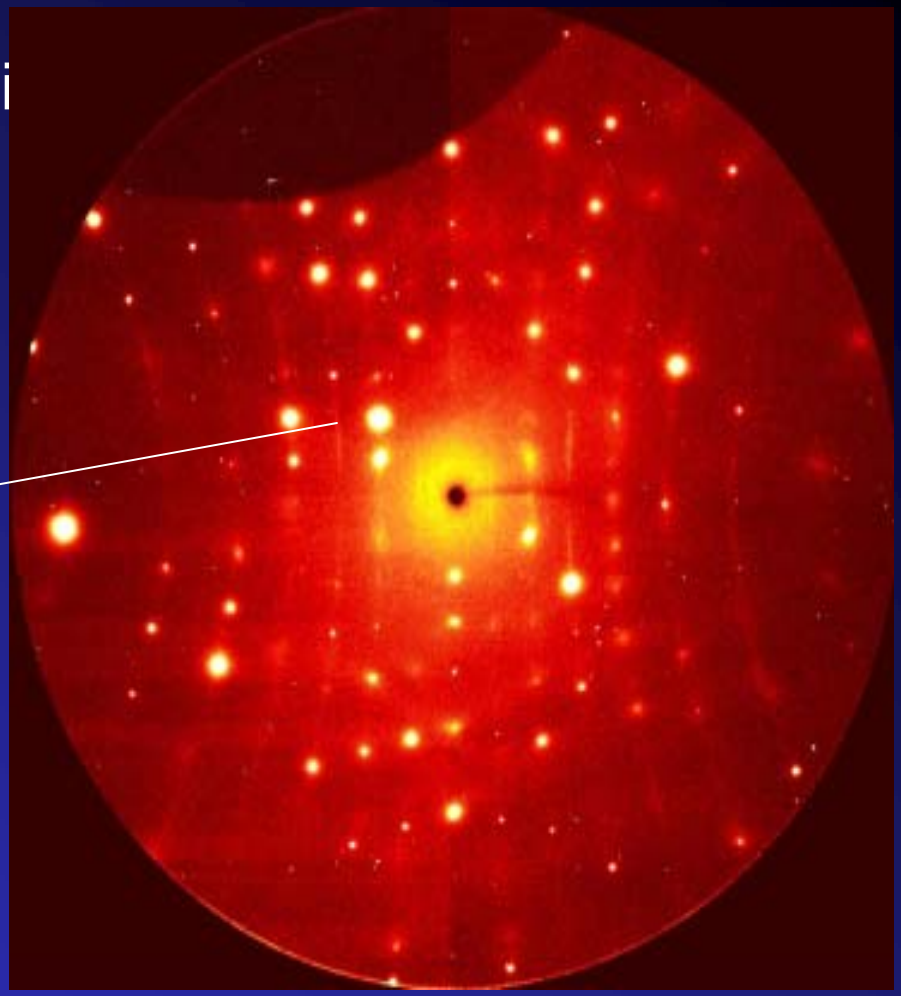
1D local order exist at the very first step : correlation/diffuse scattering??

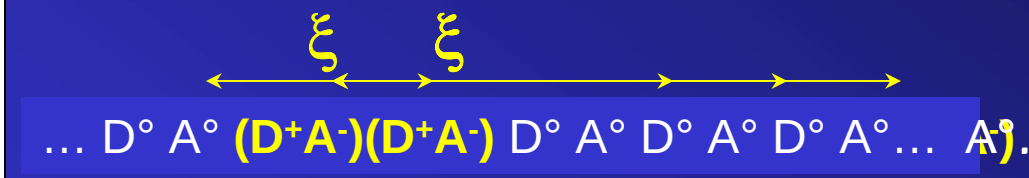
C. Siders and A. Cavalleri, Science 300 (2003)

Importance of the time resoluti and x-ray flux

Ex : signal dependence
with the size of the excitations







E. Collet et al, *Europhys. Lett.* 57 (2002)

CONCLUSIONS AND PERSPECTIVES

- **X-ray diffraction :**

  photo-induced structural change: intra and inter-molecular reorganization

- **Materials :**

  physical properties driven by light

- **X-ray source :**

  development of new sources and beamlines

DREAMS

- **Beyond the average structure**

  diffuse scattering associated with the local Excitons (1st step) : *flux*

- **Beyond atomic resolution**

  towards electronic resolution : *stability*

- **Towards the early events**

  coherent domino effect : *time resolution*

Next Spring,

26-30 May 2005,
University of Rennes 1 , France

Second International conference on
‘ PHOTO-INDUCED PHASE TRANSITIONS;
cooperative, non-linear and functional properties’.

Organizing committee :
Marylise Buron, Hervé Cailleau, Eric Collet, Tadeusz Luty,
GMCM, University of Rennes 1, Rennes France.

Homepage: http//www.gmcm.univ-rennes1.fr/pipt/

Topics:
-Photo-induced phase transitions.
-Photo- and femto-magnetism.
-Photo-induced coherent phonons.
-Light-induced functional materials.
-Dynamics and precursor phenomena.
-Light-driven non-thermal processes.
-Photo-induced broken gauge problems
-Photo-induced effects in nano-particles
-Ultra-fast light-induced processes in surfaces.
-Time-resolved spectroscopy and X-ray diffraction.
-Photo-induced cooperative chemical reactions in solids
-Photo-induced magnetic or electronic phase transitions
-Strongly collective and non-linear processes in excited state

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